

FABRICATION OF HIGH-ASPECT-RATIO PZT THICK FILM STRUCTURE USING SOL-GEL TECHNIQUE AND SU-8 PHOTORESIST

Nobuyuki Futai, Kiyoshi Matsumoto and Isao Shimoyama

Department of Mechano-Informatics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Tel: +81-3-5841-6318, Fax: +81-3-3818-0835, E-mail: {futai, matsu, isao}@leopard.t.u-tokyo.ac.jp

ABSTRACT

An optimized sol-gel process and an SU-8 photoresist were used to produce thick and high-aspect-ratio lead zirconate titanate (PZT) structures on platinized silicon substrates. The fabrication process involved single coating, lapping of the gel, and rapid firing. The PZT structures made with this new process were crack-free and had good crystallinity. Their XRD patterns and ferroelectric properties showed that the structures were high quality PZT. Values of relative permittivity and dielectric loss of the PZT were over 300 and 0.03, respectively. The structures had thickness of 20 μm or higher, and had aspect ratio of over one.

INTRODUCTION

Demand for lead zirconate titanate (PZT) films is increasing in micro electromechanical systems (MEMS), such as in force (or pressure/acceleration) sensors, micro actuators, optical devices, and large capacitors for micro powering systems [1]. Although many MEMS applications require thick (over 1 μm) PZT films, the thickness of PZT films used in MEMS is usually less than 1 μm [1, 2].

Various methods of high-aspect-ratio and/or selective fabrication of PZT structures have been proposed, such as silicon molding of PZT slurry [5] and cutting of PZT substrates [6, 7]. However, these methods are not very practical because they need highly specialized equipment and have low compatibility with conventional IC/MEMS processes.

A better alternative for selective/high-aspect-ratio fabrication of metal oxide structures is the sol-gel technique which only requires simple and low temperature process. However, even with this method, it has been difficult to fabricate dense, crack-free PZT thick patterned film with a few coatings. Thicker PZT films required time-consuming multiple coatings [1, 3]. Selective sol-gel film processes such as etching of PZT sol [4] were low-aspect-ratio patterning processes.

The present paper proposes a simple fabrication of high-aspect-ratio PZT structures with a single coat and using a thick photoresist SU-8. The SU-8 makes high-aspect-ratio patterns easily. It has good chemical compatibility and large thermal shrinkage. We also optimized the concentration, coating method, and drying/firing conditions of PZT precursor solution to avoid cracks/voids in the PZT structures and to prevent SU-8 patterns from breaking PZT gels.

Table 1. Chemicals used for the PZT precursor solution.

Chemicals	Quantities
Lead acetate dehydrated	5.856 g
Zirconium tetra-n-butoxide	3.079 g
Titanium tetra-n-butoxide	2.377 g
Acetic acid	6 ml
Methanol	3 ml
Water	1 ml

PREPARATION OF PRECURSOR

The fabrication of thick film using sol-gel method requires precursor solution of high concentration, high stability, high boiling point, and low carbon content. We prepared PZT precursor solution based on the acetic acid-based method with “inverted mixing order (IMO)” of alkoxides [9].

Table 1 shows the chemicals used for the preparation of 0.8 M solution for PZT with the molar ratio of Pb : Zr : Ti = 1.2 : 0.53 : 0.47.

Figure 1 is the flow diagram showing the steps of preparation. We have used a dry box and the precursor solution was prepared in a nitrogen atmosphere.

FABRICATION

The fabrication processes are shown in Fig.2.

- (1) Pt (100 nm) / Ti (30 nm) bottom layers are deposited on a silicon wafer (thickness: 250 μm) using a vacuum deposition. An SU-8 25 layer is patterned to form circular apertures. The thickness of the SU-8 layer is 50 μm . Diameters of apertures are 40 μm , 80 μm , and 180 μm , respectively.
- (2) The PZT solution is dispensed on the SU-8 layer, filtered with a 0.2 μm syringe filter. Then, the wafer with PZT sol is dried in a sealed container at room temperature to gelatinize the sol.
- (3) PZT wet gel is prebaked at 140 $^{\circ}\text{C}$ prior to lapping.
- (4) The wafer is lapped using a urethane foam pad. Isopropyl alcohol (IPA) is used as solvent and lubricant. Excessive wet gel on the SU-8 layer is scraped off. This procedure prevents the gel in the SU-8 mold from cracking when the gel gets dry.

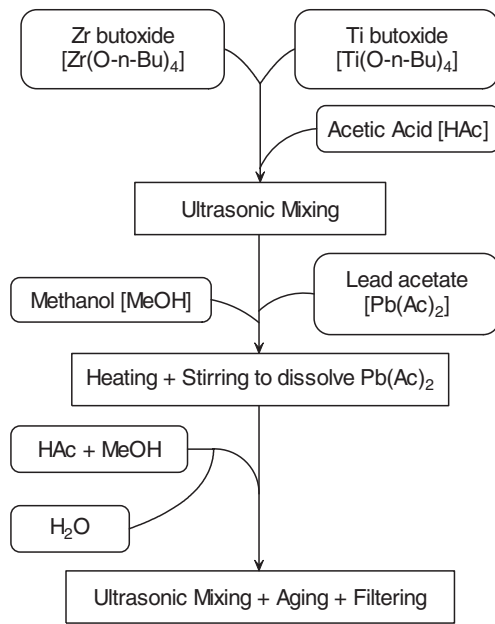


Figure 1. Preparation of the PZT precursor solution.

- (5) The gel is fired on a hotplate at 350 °C for 10 min. At this moment, the gel changes into amorphous solid of PZT, and the SU-8 layer separates from the PZT structures. Thus, SU-8 molds do not bond with the PZT structures while firing. Then, heat treatment is applied to the wafer. Its profile is shown in Figure 3.
- (6) Finally, the sample is annealed at 600 °C for 20 min. It is also a removal process of the residual of SU-8.

One critical point of the process is the preheat of the wafer with the wet gel. The wafer must be covered during heating and cooling. While cooling, the wafer must left still until the hotplate goes back to room temperature. Slight thermal shock can cause cracking in the gel.

The effects at temperature set points (A–D), shown in Figure 3, are as follows:

- A: Temperature for pyrolysis of alkoxides/lead acetate and partial carbonization of SU-8.
- B: Large deformation of residual SU-8. It still remains to be carbonized.
- C: Ashing of SU-8, accompanied with another large deformation of the SU-8 layer.
- D: Annealing of the amorphous PZT for crystallization.

FABRICATED STRUCTURES

Figure 4 shows the micrograph of fabricated PZT structures. The diameter of the SU-8 molds used to fabricate the PZT structures in Figure 4 is 200 μm . Optical micrograph of

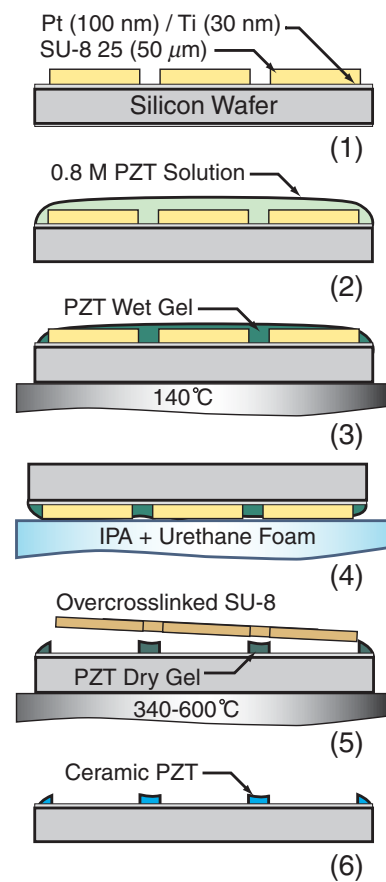


Figure 2. Fabrication processes of the PZT structures.

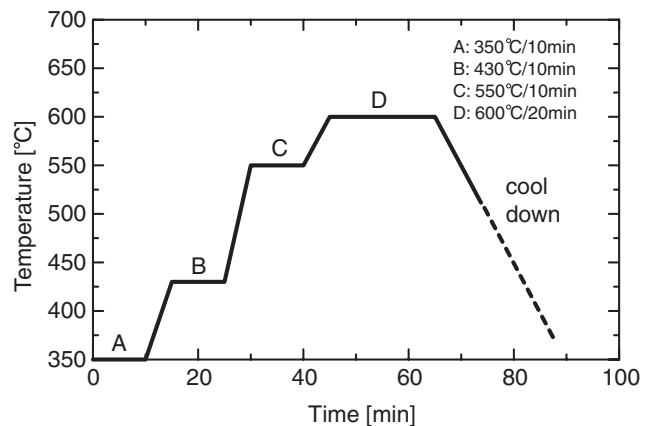


Figure 3. Heat treatment profile of the wafer.

the PZT structures shows that the structures are crack-free. We can use these structures as capacitors and actuators by adding upper electrodes of silver paste. As shown in the SEM micrograph, the thickness of these structures is over 20 μm .

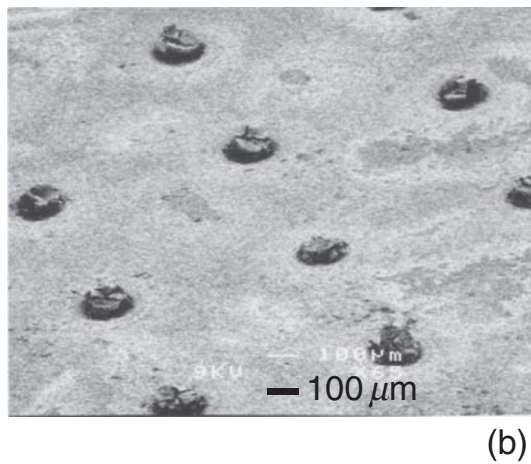
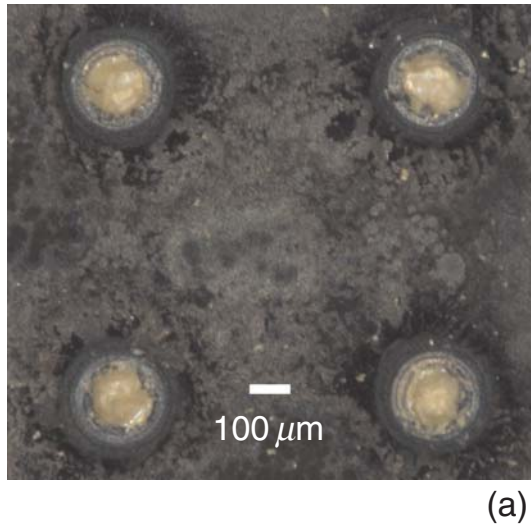


Figure 4. Micrographs of the PZT structures.

Figure 5 shows the SEM close-up micrograph of fabricated PZT structures. The top surfaces of the fabricated structures are not smooth because they are made from gel-state matter. As shown in Figure 5(b), when the structure has surfaces of large area, we can see some flashes and shallow clefts on the surfaces due to surface tension of precursor solution. However, they are not cracks of entire structure and can be easily removed by conventional lapping processes.

CHARACTERISTICS OF PZT

The phases and the crystal orientations of the PZT were measured using a Rigaku RINT2000 X-ray diffractometer (XRD). The XRD pattern of the PZT structure is shown in Fig.6. We can observe typical peaks associated with perovskite-type PZT phase. Preferential (100), (110) and (111) orientations were dominant in the PZT. However, some amount of pyrochlore phase can be observed because of long firing time around 350 °C and 430 °C in order to

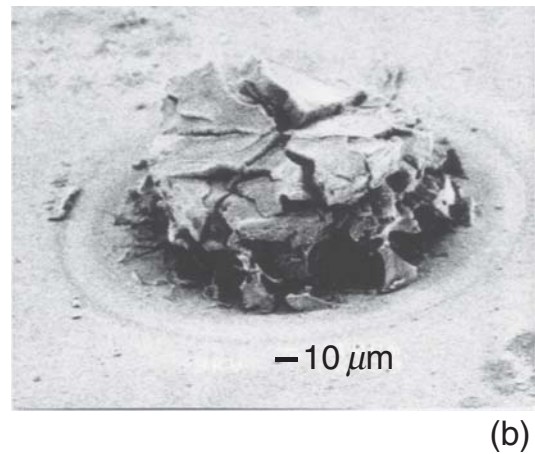
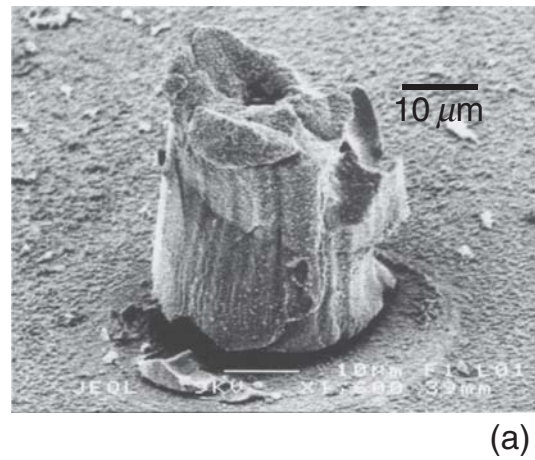


Figure 5. SEM close-up micrographs of the PZT structure. The diameters of the SU-8 molds are (a) 40 μm; (b) 180 μm.

make high-aspect-ratio structures.

Dielectric constant and dielectric loss value were measured with a HIOKI 3532 LCR hitester. Dielectric constant and dielectric loss were over 300 and 0.03, respectively.

Figure 7 shows the ferroelectric hysteresis loop at 100 Hz measured using a modified Sawyer-Tower circuit. This hysteresis loop shows that the film is ferroelectric lead zirconate titanate.

CONCLUSIONS

This paper showed that single coat sol-gel method, which has high compatibility with IC/MEMS processes, allows easier production of high-aspect-ratio PZT microstructures. The process involved a SU-8 thick photoresist, chemical-mechanical polishing (CMP) of PZT sol, and continuous direct heating.

Important factors involved in the process are 1) stability of precursor solution, 2) preheat temperature of PZT sol, and 3) firing profile of PZT composition and 'safety' release

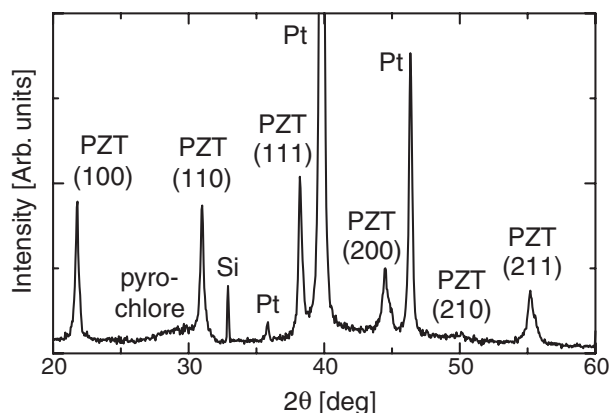


Figure 6. XRD pattern of the fabricated PZT.

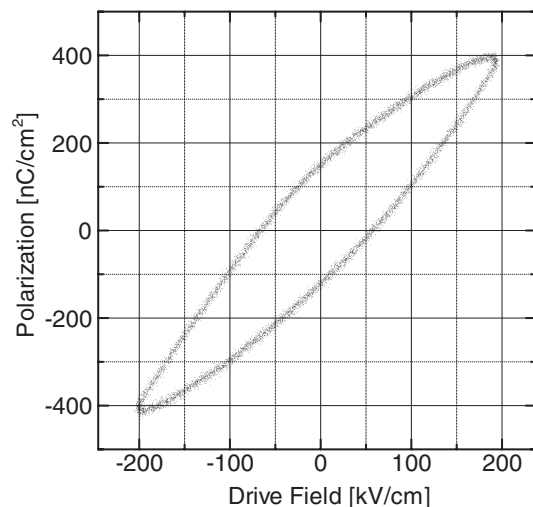


Figure 7. Ferroelectric hysteresis loop of the PZT structures.

of the SU-8 layer. Deformation of the PZT structures and residue of the SU-8 layer can be problematic, but it can be easily avoided by performing another lapping/etching process.

The PZT structures fabricated with this new process were crack-free and had good crystallinity. Their XRD patterns and ferroelectric properties showed that the structures were high quality PZT. With this method, we can provide useful PZT structures to existing ICs and MEMS. Moreover, the method we developed seems applicable to metal oxides other than PZT as well.

ACKNOWLEDGMENTS

We wish to thank Dr. Zhan-jie Wang at Tohoku University, Dr. Jiang-wen Wan and Dr. Ryutaro Maeda at National Institute of Advanced Industrial Science and Technology

(AIST) for fabrication and measurements of sol-gel based PZT films.

Photolithography masks were fabricated using EB lithography apparatus of VLSI Design and Education Center (VDEC), the University of Tokyo.

REFERENCES

- [1] P. Muralt, PZT thin films for microsensors and actuators: Where do we stand?, *IEEE Trans. of UFFC*, Vol. 47, No. 4, pp. 903–915, 2000.
- [2] Y. Yee, J. U Bu, M. Ha, J. Choi, H. Oh, S. Lee, and H. Nam, Fabrication and characterization of a PZT actuated micromirror with two-axis rotational motion for free space optics, *Proc. of IEEE MEMS 2001*, pp. 317–324, 2001.
- [3] C. Lee, T. Itoh, and T. Suga, Micromachined piezoelectric force sensors based on PZT thin films, *IEEE Trans. of UFFC*, Vol. 43, No. 4, pp. 553–559, 1996.
- [4] T. Omori, H. Makita, M. Takamatsu, K. Hashimoto and M. Yamaguchi, Selective area PZT-preparation by sol-gel method, *Proc. of 1999 IEEE Ultrasonics Symposium*, pp. 995–998, 1999.
- [5] S. N. Wang, K. Wakabayashi, J. F. Li and M. Esashi, Batch fabrication of stacked piezoelectric microactuators by using silicon mold process, *Proc. of Transducer '99*, pp. 1762–1763, 1999.
- [6] G. Suzuki and M. Esashi, Planer fabrication of multilayer piezoelectric actuator by groove cutting and electroplating, *Proc. of IEEE MEMS 2000*, pp. 46–51, 2000.
- [7] S. Ballandras, M. Wilm, M. Gijs, A. Sayah, E. Andrey, J. J. Boy, L. Robert, J. C. Baudouy, W. Daniau and V. Laude, Periodic arrays of transducers built using sand blasting and ultrasound micromachining techniques for the fabrication of piezocomposite materials, *Proc. of 2001 IEEE Ultrasonics Symposium*, 2001.
- [8] G. Yi, Z. Wu, and M. Sayer, Preparation of Pb(Zr, Ti)O₃ thin films by sol gel processing: Electrical, and electro-optic properties, *J. Appl. Phys.*, Vol. 64, No. 5, pp. 2717–2724, 1988.
- [9] T. Olding, B. Leclerc and M. Sayer, Processing of multilayer PZT coatings for device purposes, *Integrated Ferroelectrics*, Vol. 26, pp. 225–241, 1999.
- [10] Y. L. Tu and S. J. Milne, A study of the effects of process variables on the properties of PZT films produced by a single-layer sol-gel technique, *J. of Materials Science*, Vol. 30, pp. 2507–2516, 1995.